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# Inductive Heating Assisted-Catalytic Dehydrogenation of Tetralin as a Hydrogen Source for Downhole Catalytic Upgrading of Heavy Oil

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## Abstract

The Toe-to-Heel Air Injection (THAI) combined with a catalytic add-on (CAPRI, CAtalytic upgrading PRocess In-situ) have been a subject of investigation since 2002. The major challenges have been catalyst deactivation due to coke deposition and low temperatures ( $\sim 300$  °C) of the mobilised hot oil flowing over the catalyst packing around the horizontal well. Tetralin has been used to suppress coke formation and also improve upgraded oil quality due to its hydrogen-donor capability. Herein, inductive heating (IH) incorporated to the horizontal production well is investigated as one means to resolve the temperature shortfall. The effect of reaction temperature on tetralin dehydrogenation and hydrogen evolution over NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst at 250–350 °C, catalyst-to-steel ball ratio (70% v/v), 18 bar and 0.75 h<sup>-1</sup> was investigated. As temperature increased from 250 to 350 °C, tetralin conversion increased from 40 to 88% while liberated hydrogen increased from 0.36 to 0.88 mol based on 0.61 mol of tetralin used. The evolved hydrogen in situ hydrogenated unreacted tetralin to *trans* and *cis*-decalins with the selectivity of *cis*-decalin slightly more at 250 °C while at 300–350 °C *trans*-decalin showed superior selectivity. With IH the catalyst bed temperature was closer to the desired temperature (300 °C) with a mean of 299.2 °C while conventional heating is 294.3 °C. This thermal advantage and the nonthermal effect from electromagnetic field under IH improved catalytic activity and reaction rate, though coke formation increased.

**Keywords** Inductive heating · Catalytic upgrading · Tetralin · Hydrogen

## 1 Introduction

Worldwide transportation energy consumption was forecast as 151 quadrillion Btu in 2040, which represents an increase of 44 quadrillion Btu from 2015 [1]. As the world's demand for transportation fuels is rising, securing adequate supply is the real challenge. The major source of supply, light crude oil, has peaked and is declining in reserves [2, 3]. Heavy oil and bitumen hold about 70% of the world's oil reserves, estimated at 13 trillion barrels [3], which has shifted attention towards developing extraction and upgrading technologies for them. This is because under reservoir conditions, heavy oils cannot flow like light oil and, so resist flow toward the production well as they are highly-viscous and possess low

American Petroleum Institute (API) gravity. Hence, upon production, additional costs are incurred for pipeline transport and surface upgrading.

The commonly used extraction methods are steam injections such as cyclic steam stimulation and Steam Assisted Gravity Drainage (SAGD). However, alternatives include in situ combustion and Toe-to-Heel Air Injection (THAI) process. For simultaneous extraction and downhole upgrading of heavy oils, a catalytic add-on (CAPRI, CAtalytic upgrading PRocess In-situ) was combined with THAI [2, 4]. In this process, about 10–15% of the original oil in place is combusted and the developed combustion front advances from toe to heel of the horizontal production well through continuous air injection via a vertical injection well. The high thermal energy released from the combustion reaction between the oil and injected air increases the temperatures of the combustion front in the range of 400–700 °C, which mobilizes the rest of the oil toward the horizontal production well aided by gravity [4]. As the mobilized hot oil ahead of the combustion front flows over the catalyst packing around the horizontal well additional downhole upgrading occurs

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[2–4]. Previous studies found that the actual temperature of the mobilized hot oil passing through the catalyst packing around the horizontal well in the THAI process may not exceed 300 °C [5, 6]. However, in other studies it was found that a temperature of about 425 °C is needed to maximise catalytic upgrading [2, 3, 7, 8]. To achieve the needed 425 °C or more, inductive heating (IH) has been proposed in this study as a means to provide the additional heating required for optimum catalytic upgrading. IH has previously been integrated with a batch reactor in which paramagnetic nanoparticles such as iron coated with silica were used to convert electromagnetic field to heat for organic synthesis process [9]. Also, applied to fluidized bed system by co-fluidization of conductive particles which are chemically inert in order to heat the process [10]. Furthermore, IH has been incorporated with steam-assisted gravity drainage (SAGD) to expand the steam chamber and improve oil recovery [11]. With the aid of composite catalyst pellets consisting of a conductive component and a catalytic material [12, 13], or a mixed bed of catalyst and conducting susceptors [10], an inductive system can be applied to generate thermal energy inside the reactor. Herein, a laboratory-scale inductive heated reactor was developed, and a mixed bed of catalyst and chemically inert steel balls susceptors used to convert electromagnetic field into heat, which increases the temperature of the catalytic bed to the reaction temperatures. This is done with an emphasis on applications in THAI–CAPRI process for heavy oil recovery and in situ upgrading. The heat is generated rapidly in the area of interest; thus minimising heat lost, lowering energy costs, maintaining uniform temperature across the catalytic bed and ensuring controllability [10, 13].

Another challenge with in situ catalytic upgrading of heavy oils using THAI–CAPRI is large coke deposition on the catalyst results in rapid deactivation, bed plugging and low quality of upgraded oil [14, 15]. Coke formation can be suppressed when the catalytic upgrading is carried out under a hydrogen rich environment [15]. The difficulty, safety and cost associated with transporting hydrogen gas itself into the reservoir have shifted attention to hydrogen-donor solvents such as polycyclic compounds (i.e., cyclohexane, decalin and tetralin) [16]. These organic liquids potentially store and transport hydrogen in a safer and less challenging manner when compared to external transport of hydrogen gas itself into the reservoir. Also, they can easily be injected into the reservoir using either the vertical injection or horizontal production wells of the THAI–CAPRI process. These polycyclic compounds can hydrogenate–dehydrogenate in the upgrading mixture, and the evolved hydrogen has been found to improve the quality of upgraded oil and minimise coke formation by halting polymerisation of free radicals from cracked heavy molecules. The dehydrogenation of tetralin to naphthalene

can be used as a hydrogen source to promote in situ hydrocracking and hydrogenation reactions in the catalytic add-on (CAPRI) to THAI. Hart et al. [16] reported that the use of cyclohexane as hydrogen-donor solvent for downhole catalytic upgrading of heavy oil suppressed coke formation. Many studies have reported the use of tetralin as H-donor solvent [14, 17, 18], and the findings showed that coke formation is suppressed and upgraded oil quality improved. However, studies on the quantification of liberated hydrogen from tetralin are very limited even though the mechanism of hydrogen evolution through dehydrogenation of tetralin to naphthalene is well-known. These polycyclic compounds have shown the ability to suppress coke formation which is usually attributed to the participation of the evolved hydrogen in the upgrading process.

The dehydrogenation of tetralin to liberate hydrogen and produce naphthalene is faced with two challenges. The first is that dehydrogenation is an endothermic reaction that requires high temperature, and the temperature of the hot oil passing over the catalyst bed in the THAI–CAPRI is in the range of only 100 to 300 °C [6], which is non-uniform and also below 425 °C needed for effective catalytic upgrading. The other is that the produced naphthalene will compete with the heavy oil molecules for adsorption on the catalyst active sites [19, 20]. Since the catalyst bed under IH functions as a heat generator, the first challenge can be addressed unlike conventional heating (CH) system where the catalyst bed acts as a heat sink. The catalytic dehydrogenation of tetralin to naphthalene is commonly performed over Pd or Pt supported catalyst at high temperature [21–23]. However, Pd or Pt cannot withstand the sulphur content in heavy oil. Hence, transition metals such as Ni, Co and Mo supported on alumina and/or silica are commonly used in catalytic upgrading of heavy oil and were used in this study [24, 25]. In this study, a laboratory-scale inductive heated reactor to be combined with THAI–CAPRI process for heavy oil recovery and in situ upgrading was developed. Heat was generated inside the mixed bed of catalyst (NiMo/Al<sub>2</sub>O<sub>3</sub>) pellets and steel balls of size 3 mm which convert electromagnetic field into heat. It has been demonstrated that the mixture of NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst and steel balls (catalyst-to-steel balls ratio, CTSBR 70% v/v) inside the CAPRI reactor can rapidly heat the catalyst to 425 °C in about 25 min and enhance catalytic transformation compare to CH. The amount of hydrogen obtainable from tetralin as hydrogen-donor solvent for catalytic upgrading of heavy oil using hydrotreating (HDT) catalyst NiMo/Al<sub>2</sub>O<sub>3</sub> was experimentally verified. The effect of reaction temperature on hydrogen evolution was examined. Furthermore, a comparative study was carried out on tetralin conversion and hydrogen evolution when the mixed bed of catalyst was heated inductively with steel balls and conventionally at varying reaction temperatures. First-order kinetics and a plug flow model were used to estimate the

apparent rate constant and apparent activation energy of the reaction in both inductive and conventional heated systems.

## 2 Experimental

### 2.1 Materials

Commercial HDT catalyst  $\text{NiMo}/\text{Al}_2\text{O}_3$  quadra-lobe shaped (Akzo-Nobel) was used. The tetralin (99.5% purity) used in this study was purchased from Sigma Aldrich, UK and *n*-hexadecane (99%, Alfa Aesar, UK) as solvent. 80 g of tetralin was added to 1 L of *n*-hexadecane stirred for 2 h by magnetic stirrer to form a solution used for the reaction.

### 2.2 CAPRI Reactor

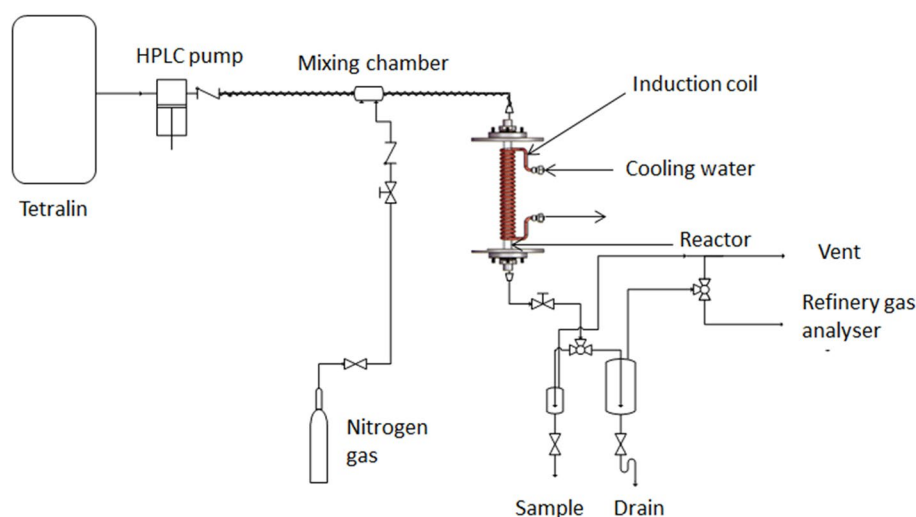
The inductive heated CAPRI reactor to be combined with the horizontal production well of the THAI process was replicated by a fixed-bed reactor, which comprises of a quartz glass tube (length 440 mm and diameters 20 mm i.d., 40 mm o.d.) where an induction coil was wrapped around it. The schematic diagram of the experimental reactor is shown in Fig. 1. The bed of catalyst was a mixture of  $\text{NiMo}/\text{Al}_2\text{O}_3$  pellets and steels balls of 3 mm. The steel balls function as susceptors that convert electromagnetic field into heat to inductively heat the catalyst bed. The top and bottom of the bed was occupied by chemically inert glass beads of size 5 mm. A thermocouple (type k) was inserted from the bottom to the centre of the catalytic bed to measure temperature. The experiment was carried out at the percolation threshold of 70% (v/v) CTSBR (this is the minimum amount of steel balls required to achieve a thermal conducting pathway throughout the bed), pressure 18 barg, LHSV  $0.75\text{ h}^{-1}$ , temperature  $250\text{--}380\text{ }^\circ\text{C}$  and gas flow rate of  $200\text{ mL min}^{-1}$  ( $\text{N}_2$ ). The liquid reactant was pumped through using a HPLC

pump, preheated to  $190\text{ }^\circ\text{C}$  and introduced in a downward flow mode into the reactor. This simulates the mobile oil zone and the gravity drainage of the hot oil passing over the catalyst bed around the horizontal well of the THAI process. The dehydrogenation reaction was carried out under a nitrogen environment, and the pressure inside the reactor was controlled using a back pressure regulator. An identical experimental configuration was used for the CH experiment as control in which the heat is generated by an external electrical furnace. Before the start of experiment, the catalyst was reduced in a hydrogen gas atmosphere at a temperature of  $300\text{ }^\circ\text{C}$ , pressure of 5 bar and flowrate of  $20\text{ mL min}^{-1}$ .

### 2.3 Analytical

The liquid product was analysed using a FID equipped gas chromatograph (GC) 6890N and a capillary column HP-5 ( $30\text{ m} \times 0.320\text{ mm} \times 0.25\text{ }\mu\text{m}$ ). The catalyst surface area, pore volume and size were determined by nitrogen adsorption technique using Micromeritics Analytical Instrument ASAP® 2010, using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) equations according to ASTM C1274. Bruker AXS GmbH (D8 Advanced XRD, Karlsruhe, Germany) was used to collect the X-ray diffraction (XRD) data of the catalyst using  $\text{Cu K}\alpha$  radiation from  $10$  to  $80^\circ 2\theta$  and a step width size of  $0.025^\circ$ . Consequently, Hitachi TM3030Plus tabletop scanning electron microscope equipped energy dispersive X-ray spectroscopy (EDS) was used to examine the morphology of catalyst and quantify the elemental composition. Micromeritics AutoChem II 2920 analyser was used to determine the number and the strength of the catalyst acid sites through temperature programmed desorption using *tert*-butylamine [ $(\text{CH}_3)_3\text{CNH}_2$ ]. The coke deposited on the catalyst after reaction was determined using a thermogravimetric analyser, TGA (TG 209 F1 Iris® instrument, Netzsch-Geratebau GmbH) under air atmosphere with

**Fig. 1** Inductive heated-catalytic reactor



flowrate 50 mL min<sup>-1</sup>, ramp temperature 25 to 900 °C step increase 10 °C min<sup>-1</sup> and held at 900 °C for 8 min. The gaseous product was analysed online using Agilent 7890A GC configured as a refinery gas analyzer.

### 3 Results and Discussion

A flowchart of the tetralin dehydrogenation is shown in reaction Scheme 1. The amount of hydrogen liberated from tetralin due to dehydrogenation to naphthalene, the conversion of tetralin, and the respective selectivity of naphthalene, *trans* and *cis*-decalins, and fixed-bed reaction kinetic are presented and discussion in Sects. 3.1 to 3.4. The effect of electromagnetic field and the thermal advantage due to IH on the catalyst performance evaluated against CH is presented and discussed in Sect. 3.5.

The conversion of tetralin and the respective selectivity of the dehydrogenation products are defined by the equations.

The conversion of tetralin:

$$\text{Conversion} = \frac{C_{\text{Tetralin}}^0 - C_{\text{Tetralin}}}{C_{\text{Tetralin}}^0} \times 100\%.$$

The selectivity of compound i:

$$\text{Selectivity } (S_i) = \frac{C_i}{\sum_{i=1}^n C_i} \times 100\%,$$

where  $C_{\text{Tetralin}}^0$ ,  $C_{\text{Tetralin}}$  are the initial and final concentration of tetralin and  $C_i$  is the concentration for compound i.

#### 3.1 Catalyst Characterization

The physicochemical properties of the NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst used are shown in Table 1. Figure 2 shows the nitrogen adsorption–desorption isotherm (a) and the XRD (b). The nitrogen adsorption–desorption isotherm curve (Fig. 2a) shows a big hysteresis loop between the adsorption and desorption isotherms, signifying type IV isotherm and mesoporous characteristics. The XRD pattern reveals two prominent peaks of cubic  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 46° and 67° (Fig. 2b). The presence of peaks at 2 $\theta$  of 37.3° indicates common Ni

**Table 1** Physicochemical properties of NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst

Parameter	Values
Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	237.74
Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	0.57
Pore diameter (nm)	8.8
Ni (wt%)	7
Mo (wt%)	21
Weak acid site at 280 °C [mmol adsorbed (CH <sub>3</sub> ) <sub>3</sub> CNH <sub>2</sub> g <sup>-1</sup> ]	0.62
Strong acid site at 480 °C [mmol adsorbed (CH <sub>3</sub> ) <sub>3</sub> CNH <sub>2</sub> g <sup>-1</sup> ]	0.12

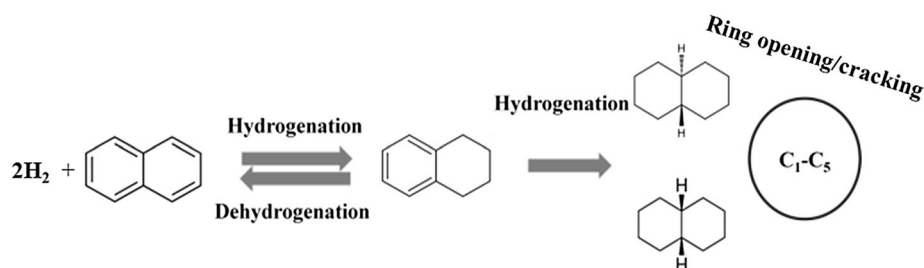
oxides (NiO and Ni<sub>2</sub>O<sub>3</sub>). The small peak that appears at 33.6° can be attributed to MoO<sub>3</sub>.

The SEM micrograph and EDS of the catalyst are shown in Fig. 3, displaying the surface morphology of the NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst. The active phase species Ni and Mo are well-dispersed on the surface of the alumina support as shown in the elemental mapping (Fig. 3c, d) with 7.3% Ni and 20.5% Mo, which implies the ratio of Ni to Mo is approximately 1:3. This ratio of promoter (Ni) to active element (Mo) is within a typical HDT catalyst.

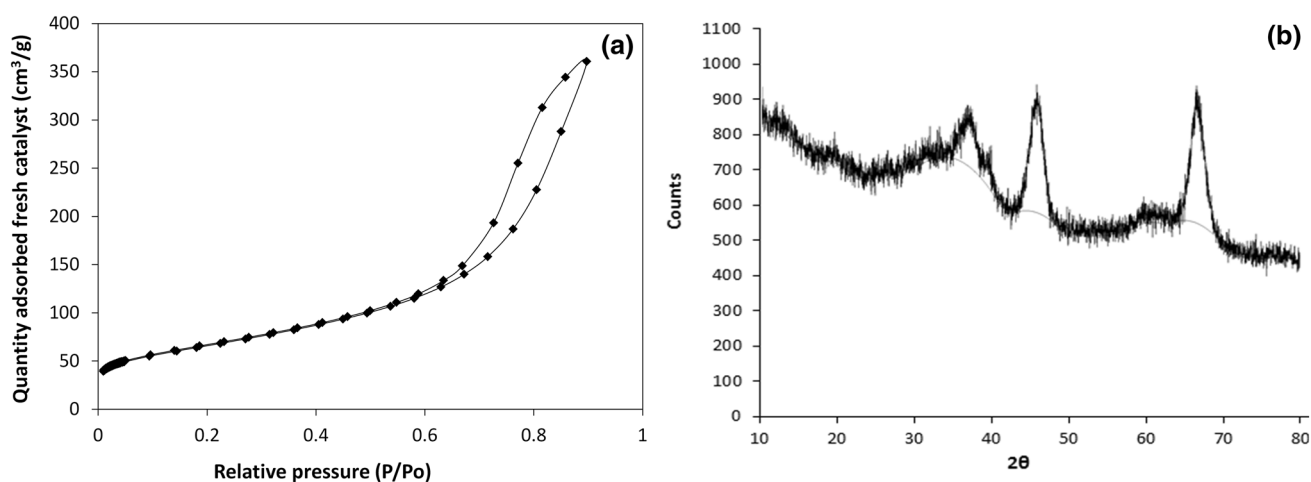
#### 3.2 Catalyst Bed Temperature Profiles

The design of the inductive heated reactor makes it technically challenging to incorporate an infrared radiation thermometer to measure the temperature of the catalytic bed. However, it has been reported that the interference of electromagnetic field with the thermocouple can be significantly reduced by shielding for a frequency of 50 Hz [26]. The measured temperature profiles of the catalyst bed for different CTSBR ranging from 30 to 70% (v/v) and the influence of magnetic field on the thermocouple reading are shown in Fig. 4. The temperature rose steeply to the desired reaction temperature in all cases, except for 70% (v/v). Since steel balls act as susceptors of electromagnetic fields and current, it is expected that the higher amount of steel balls would lead to higher heating rate due to increase interaction with the magnetic field. Hence, the volume of the bed (80 cm<sup>3</sup>) heats up more slowly as the amount of catalyst increases from 30 to 70% (v/v). This is because the catalyst is non-conductive and therefore has

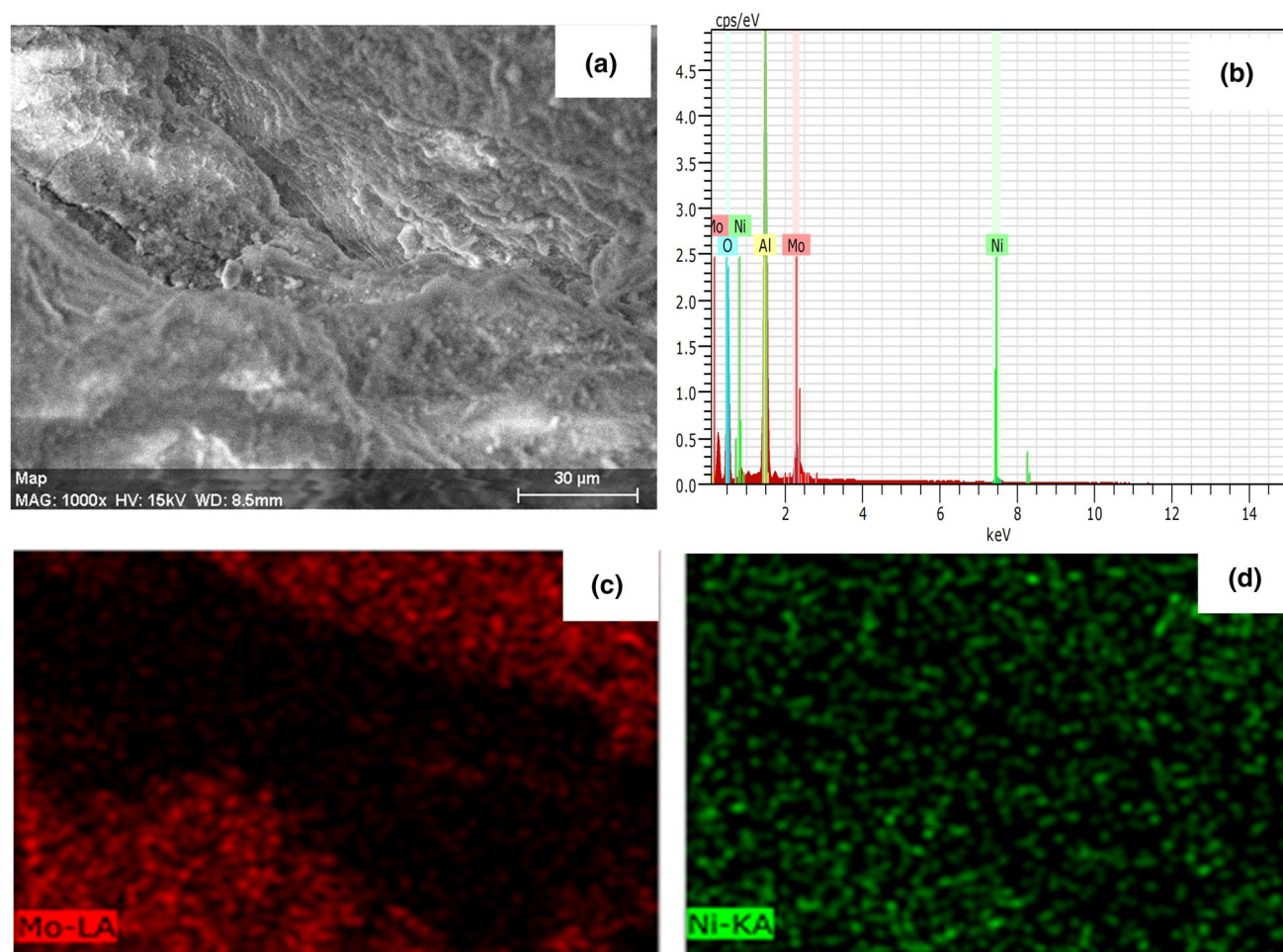
**Scheme 1** Flowchart of tetralin dehydrogenation to liberate hydrogen and produce naphthalene







**Fig. 2** Catalyst characteristics. **a** Nitrogen adsorption–desorption isotherm and **b** XRD pattern



**Fig. 3** NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst morphology. **a** SEM micrograph, **b** EDS, **c** Mo metal mapping and **d** Ni metal mapping

weak interaction with the electromagnetic fields. Hence, at CTSBR of 70% (v/v), it is clear that the impact of the electromagnetic field upon the measured temperature by the thermocouple is greatly minimized due to the protection of

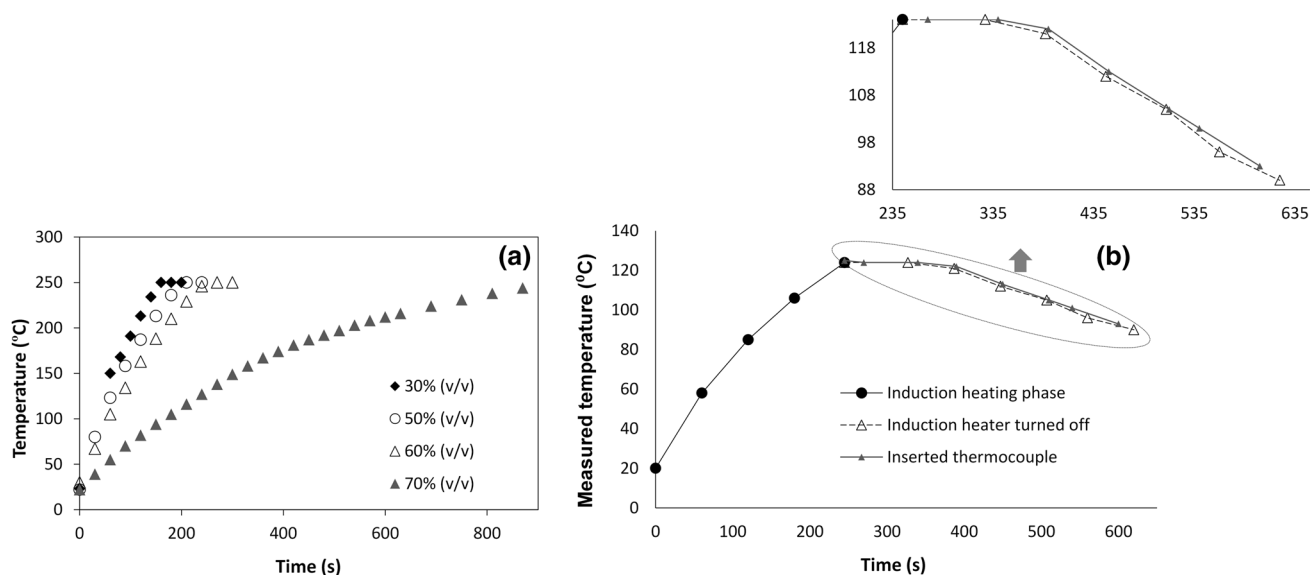
the surrounding non-conducting catalyst, the thick quartz glass tube (20 mm i.d., 40 mm o.d.) and the size of the thermocouple probe (1 mm). At 35 kHz experimental frequency and 70% CTSBR, the interaction of the magnetic field with

the thermocouple was tested (Fig. 4b). Henkel et al. [27] measured the temperature of a packed bed reactor inductively heated for pyrolysis of biomass using k-type thermocouple, once the reactor achieved the target temperature, the induction heater was switched off and the thermocouple (k-type) inserted immediately to measure the steady state temperature. In the same vein, the catalytic bed was heated inductively to 124 °C for CTSBR of 70%, and the induction heater was turned off, while the installed thermocouple response and that of the inserted thermocouple from the top were observed as shown in Fig. 4b. It can be observed that when the eddy current and magnetic field effects were eliminated by turning off the induction heater while still monitoring the temperature of the catalytic bed, the installed thermocouple maintained 124 °C for 82 s, while the inserted thermocouple started off from 125 °C, dropped to 124 °C in 25 s and maintained this temperature for 70 s before a gradual drop in measured temperature was noticed (Fig. 4b). The difference between the measured temperature by the installed and the inserted thermocouples is about 1 °C. This suggests that the sensitivity of the thermocouple to the magnetic field is significantly reduced at 70% CTSBR in addition to the non-conducting shield provided by the thick (10 mm) quartz glass tube and the distance (22 mm) of the thermocouple from the induction coil. Additionally, the power of the induction heater is adjusted by a temperature controller which design includes a signal filtering and an isolator so that there was no current path to ground. While the temperature of the catalyst pellets was 124 °C, the steel balls was 190 °C which means the major heat transfer mode is conduction due to intimate contact between them.

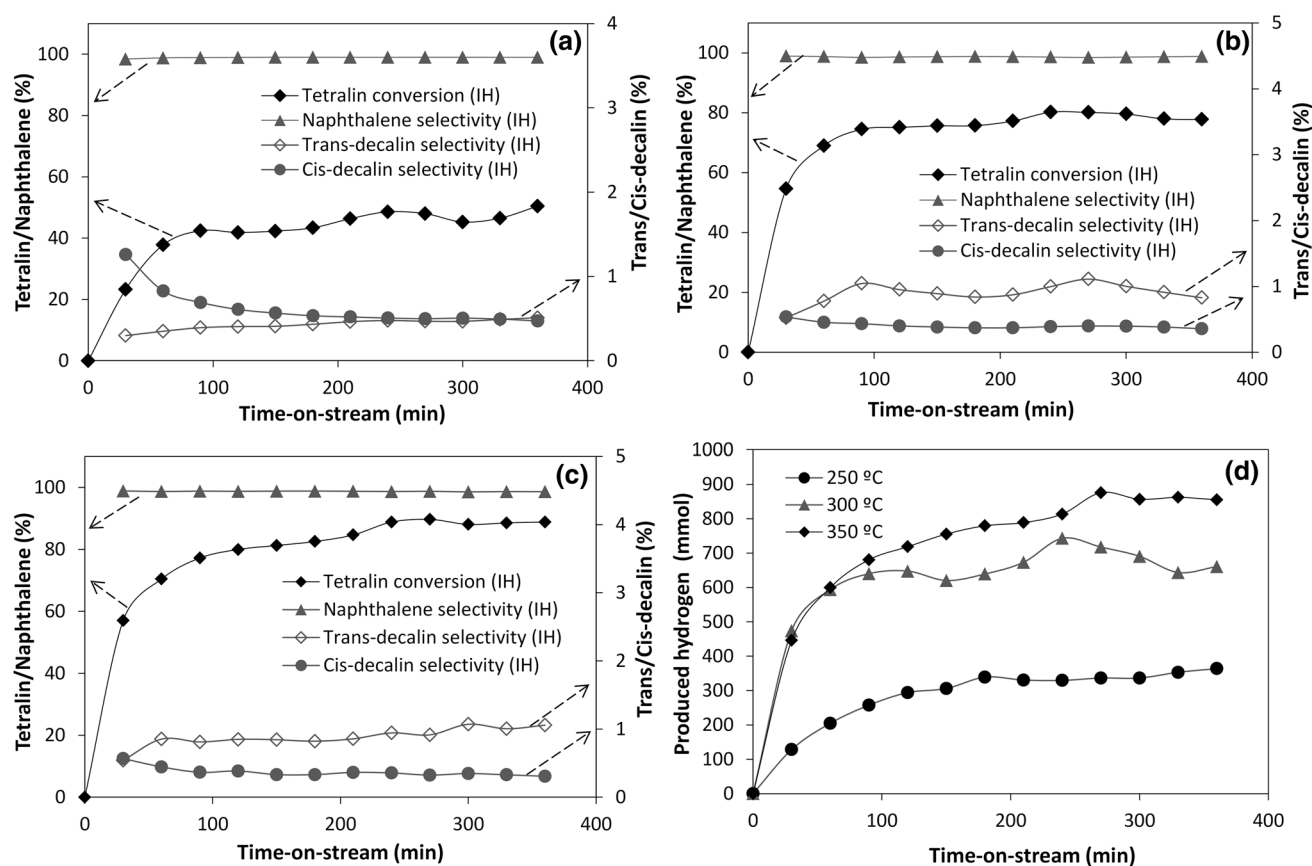
The measured temperature by the thermocouple is approximately that of the heated catalytic bed, the difference between 60% and 70% (v/v) catalyst/steel ratio affirmed this observation. Hence, the measured temperature is the heating of the steel balls majorly. When the steel balls are packed with the catalyst, they create a thermal conducting network. Therefore, the significant difference in heating rate between 60% and 70% (v/v) can be attributed to the percolation threshold for random sphere packing in 3D which is about 0.3. This means that the steel balls will form a percolating cluster and connectivity across the packed bed above 30% fractional occupancy and thus allow thermal conduction across the steel balls majorly.

### 3.3 Conversion, Selectivity and Liberated Hydrogen

The material balance of the system showed that at 350 °C, the liquid (i.e., naphthalene, tetralin, *trans* and *cis* decalins) account for about 94.4 wt% and the remainder 5.6 wt% represent deposited coke on the catalyst and the gaseous products. The active metals (i.e., Ni and Mo) are responsible for hydrogenation/dehydrogenation while the acid sites of the alumina support induce catalytic cracking [3, 15]. Figure 5 shows the conversion of tetralin, produced hydrogen and the respective selectivity toward naphthalene and *trans/cis*-decalin from the dehydrogenation of tetralin at 250, 300 and 350 °C. On the graph, the primary vertical axis shows the conversion of tetralin and the selectivity of naphthalene while the secondary vertical axis indicates the selectivity of *trans* and *cis*-decalin. At all reaction temperatures investigated, tetralin conversion increases steeply with time-on-stream and plateaus within 100 min and remained



**Fig. 4** Catalyst bed temperature **a** as a function of CTSBR (v/v) and **b** the influence of magnetic field and eddy current on the temperature reading of the thermocouple at 70% CTSBR



**Fig. 5** Tetralin dehydrogenation under induction heating at **a** 250 °C, **b** 300 °C, **c** 350 °C and **d** produced hydrogen at pressure 18 barg, LHSV 0.75 h<sup>-1</sup>, CTSBR 70% v/v and gas flow rate of 200 mL min<sup>-1</sup> (N<sub>2</sub>)

plateaued throughout the experiment, which indicates sustained catalyst activity. The observed early increase in conversion of tetralin to 100 min at all reaction temperatures investigated is as a result of catalyst start up effect, and can be attributed to the time required for steady state to be achieved in the reactor which includes time required for effective catalyst wetting and diffusion of reactants into and products out of the catalyst pore structure. The mean conversions of tetralin are as follows 43% (250 °C), 74.8% (300 °C) and 81.5% (350 °C), respectively. Thermodynamically, high temperature is necessary to provide sufficient thermal energy for this endothermic reaction; hence, the conversion of tetralin via dehydrogenation to naphthalene and hydrogen liberation increased as temperature increased from 250 to 350 °C. Chen et al. [20] observed a similar trend in tetralin conversion against time-on-stream and as reaction temperature increase. As expected, the endothermic nature of tetralin dehydrogenation process is favoured with increasing temperature.

The major product of the dehydrogenation reaction is naphthalene with selectivity of approximately 98% for all reaction temperatures investigated. The selectivity of *cis*-decalin is slightly more over the early minutes of experiment

at 250 °C. However, with time-on-stream, the ratio of *cis* to *trans*-decalin changes from 2.4:1 to 1:1 while at 300–350 °C *trans*-decalin showed superior selectivity than *cis*-decalin (ratio of 1:2). This trend is due to the instability of *cis*-decalin and its isomerisation to a more thermally stable *trans*-decalin at high temperatures.

The formation of *cis* and *trans* decalins in the dehydrogenation of tetralin is an indication of the hydrogenation reaction promoted by the evolved hydrogen mainly due to naphthalene formation. The amount of decalin produced is very small, when compared to naphthalene produced, because of the small contact time remaining after naphthalene and hydrogen have been formed. The evolved hydrogen hydrogenates some residual tetralin, under the prevailing pressure, as it trickles down the catalyst bed. The reaction is also dependent on the prevailing partial pressure of hydrogen within the reactor. Additionally, the hydrogenation of tetralin to decalin is an exothermic one which is thermodynamically unfavourable at high reaction temperatures.

The evolved hydrogen produced from tetralin dehydrogenation was estimated from the amount of naphthalene produced excluding dialin (1,2-dihydronaphthalene) product (based on reaction Scheme 1, tetralin = naphthalene + 2H<sub>2</sub>



and excluding tetralin = dialin + H<sub>2</sub>). Figure 5d shows the hydrogen production against time-on-stream over NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst at 250, 300 and 350 °C. The liberated hydrogen over the catalyst increases with time-on-stream and reaction temperature. The mean amounts of liberated hydrogen gas at the respective reaction temperatures are as follows 298.4 mmol (250 °C), 645.3 mmol (300 °C) and 752.6 mmol (350 °C). An increase in the optimum amount of liberated hydrogen from 360 to 876 mmol can be observed at 350 °C. On the other hand, the amount of tetralin converted at each reaction temperature ranges from 141 to 305 mmol (250 °C), 330 to 485 mmol (300 °C) and 345 to 543 mmol (350 °C) relative to 605 mmol of tetralin feedstock. The corresponding amounts of decalins produced are thus; at 250 °C (*trans*: 0.54–2.6 mmol, *cis*: 2.3–2.5 mmol), 300 °C (*trans*: 3.4–7.3 mmol, *cis*: 2–3.5 mmol) and 350 °C (*trans*: 1–10 mmol, *cis*: 3.65–5 mmol), respectively. This suggests that in situ hydrogenation of tetralin by the liberated hydrogen gas is negligible compared with the extent of dehydrogenation to naphthalene. This is because of temperature increase and limited hydrogen gas favours the dehydrogenation of tetralin to naphthalene as shown in Fig. 5a–c. Additionally, once tetralin dehydrogenate to hydrogen and naphthalene, the contact time between the hydrogen and the residual tetralin is insufficient to ensure reasonable conversion to *trans* and *cis* decalins in a fixed-bed continuous process.

The analysis of the gaseous product from the reaction showed the presence of 13.8 vol% (250 °C), 20.2 vol% (300 °C) and 37.6 vol% (350 °C) hydrogen. Most of this hydrogen is due to the formation of naphthalene from tetralin (selectivity of 98%) as only a negligible amount of 1,2-dihydronaphthalene was observed from the liquid product analysis. This evolved hydrogen under catalytic upgrading of heavy oil with tetralin as H-donor can promote hydrocracking and hydrogenation reactions to stabilise free hydrocarbon radicals. The formation of *trans* and *cis*-decalins in the liquid product affirmed the occurrence of the hydrogenation reaction due to the liberated hydrogen (Fig. 5a–c). The increased selectivity of *trans* and *cis*-decalins, as reaction temperature increased, can be ascribed to the increased moles of hydrogen evolved as temperature increased from 250 to 350 °C (Fig. 5d). In the light of this, hydrogen partial pressure would have increased also, thereby increasing the hydrogenation of tetralin to *trans* and *cis* decalins by the available hydrogen.

### 3.4 Fixed-Bed Reaction Kinetics

A first-order rate equation was used to represent the kinetics of the dehydrogenation of tetralin at steady-state reaction condition in the fixed-bed reactor [28]. The first-order plug

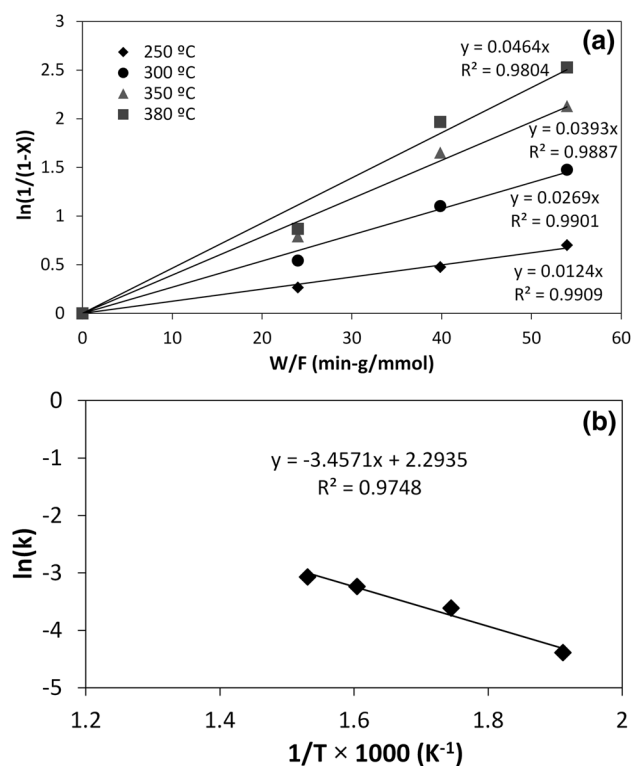
flow model shown in Eq. 1 was used to fit the experimental data.

$$\ln(1/(1-X)) = k(W/F), \quad (1)$$

where X is conversion, k apparent rate constant, W catalyst weight and F molar flow.

Figure 6a shows the plot of  $\ln(1/(1-X))$  against W/F, and Fig. 6b the Arrhenius plot. The plot fits the experimental data with approximately 0.98 (R<sup>2</sup>), which means that the dehydrogenation of tetralin is apparent first-order kinetics.

As expected an increase in reaction temperature, increases the rate of tetralin dehydrogenation, which is consistent with the results shown in Fig. 5a–c. The apparent activation energy was found as 30 kJ mol<sup>-1</sup>. It is believed that a catalyst with higher activity shows lower activation energy, this means that the reaction is mass transfer limited. This is because of the large dimensions of the catalyst particles (1.4 mm × 1.21 mm) and length (5 ± 2.1 mm) limiting the diffusion of reactants through the pores to the catalyst active sites. Additionally, the reactor internal diameter (20 mm) is significantly larger than the size of the catalyst particles. An activation energy in a similar range was reported by Chen



**Fig. 6** Tetralin dehydrogenation using Ni–Mo/Al<sub>2</sub>O<sub>3</sub> at 250, 300, 350 and 380 °C in the fixed-bed catalytic reactor with CTSBRs 35%, 50% and 70% (v/v), pressure 18 barg, LHSV 0.75 h<sup>-1</sup>, and gas flow rate of 200 mL min<sup>-1</sup> (N<sub>2</sub>): **a** first-order kinetic plot using Eq. 1 and **b** Arrhenius equation

et al. [20] for Mo supported on coal char as catalyst for tetralin dehydrogenation, though the rate constant was almost same, the activation energy obtained with NiMo/Al<sub>2</sub>O<sub>3</sub> used in this study was slightly lower.

### 3.5 Coke Formation

It is clear that high temperature is necessary to produce an appreciable amount of hydrogen through dehydrogenation of tetralin, to promote hydrogenation in downhole catalytic upgrading of heavy oil. At high temperatures, the productivity of the reaction can be constrained by catalyst deactivation due to coke deposition. Figure 7 shows the recovered catalyst TG and DTG after reaction at 250, 300 and 350 °C. The weight loss from 25 to 210 °C is the vaporisation of the residual tetralin, naphthalene and *n*-hexadecane on the catalyst, while the burn-off beyond 260 °C is due to the formed coke from dehydrogenation of tetralin for 6 h experiment [29].

The respective coke content of the catalyst after 6 h of reaction was determined as 10.2% (250 °C), 15.6% (300 °C) and 20.3% (350 °C). This represents about 5% coke increase for every 50 °C increase in reaction temperature. This increased coke formation is the result of the increased formation of the more strongly adsorbing and more condensable naphthalene compound as reaction temperature increases (Figs. 5a–c, 6a).

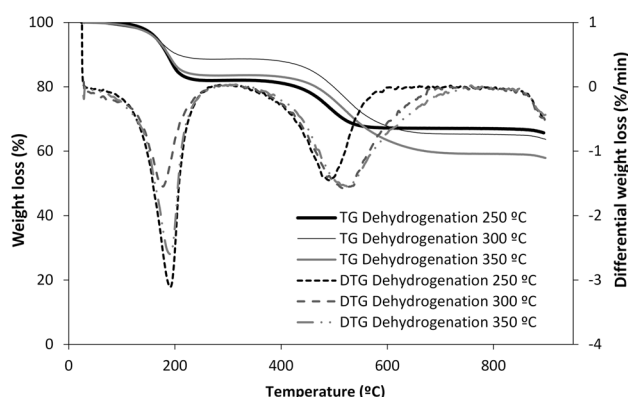
In spite of the observed coke formation, when incorporated with the THAI process, tetralin can keep the asphaltenes in the heavy oil in solution, suppressing their precipitation, polymerisation and condensation to coke while they undergo cracking [16]. The use of methane gas and cyclohexane solvent as hydrogen-donors for catalytic upgrading of heavy oil in comparison to the use of a pure hydrogen gas had been reported in the literature by the authors [16, 30]. It was found that the addition of hydrogen

gas improved the upgraded oil quality more than methane gas [30], while the use of cyclohexane solvent improved the upgraded oil quality more than hydrogen gas at cyclohexane/oil ratio of 0.08 [16]. In summary, coke formation was suppressed as follows cyclohexane > hydrogen gas > methane gas. This is because of the ability of the produced aromatic compounds due to liberation of hydrogen gas from cyclohexane to keep the asphaltene molecules solubilized inhibiting precipitation and aggregation. Potentially, the quantity of hydrogen gas liberated from tetralin dehydrogenation (Fig. 5d) can support in situ catalytic hydroprocessing of heavy oil. Since it has been proven that the liberated hydrogen gas was beneficial in capping free radicals from cracked heavy molecules such as poly-aromatic and resins in situ and consequently halt their polymerisation and condensation into coke and increase catalyst longevity [15, 31].

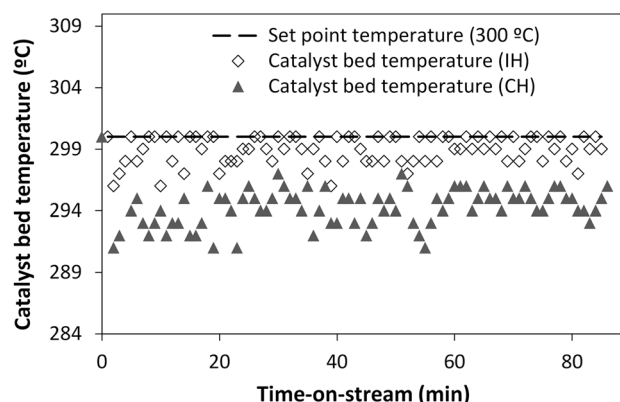
### 3.6 Inductive Against Conventional Heating

#### 3.6.1 Catalytic Bed Temperature

The temperature of the catalyst bed was measured during IH and CH with the aid of the thermocouple (type k) inserted at its centre from the bottom. Figure 8 shows the temperature of the catalyst bed for both IH and CH when the experiment was carried out at 300 °C. With IH the catalyst bed reached 300 °C temperatures in 16 min while CH takes 71 min for 70% (v/v) CTSBR. Under IH, the temperature of catalyst bed was closer to, or at, the desired temperature while for CH it drops in the range of 4–10 °C from the desired temperature. The average bed temperature was 299 °C (IH) and 294.3 °C (CH). Again, the fluctuation of the catalytic bed temperature between 296 and 300 °C in the inductive heated reactor during reaction also confirms the thermocouple experience negligible heating effect in the magnetic field.



**Fig. 7** TGA of the used catalyst after 6 h experiment at 250, 300 and 350 °C under induction heating at pressure 18 barg, LHSV 0.75 h<sup>-1</sup>, CTSBR 70% v/v and gas flow rate of 200 mL min<sup>-1</sup> (N<sub>2</sub>)

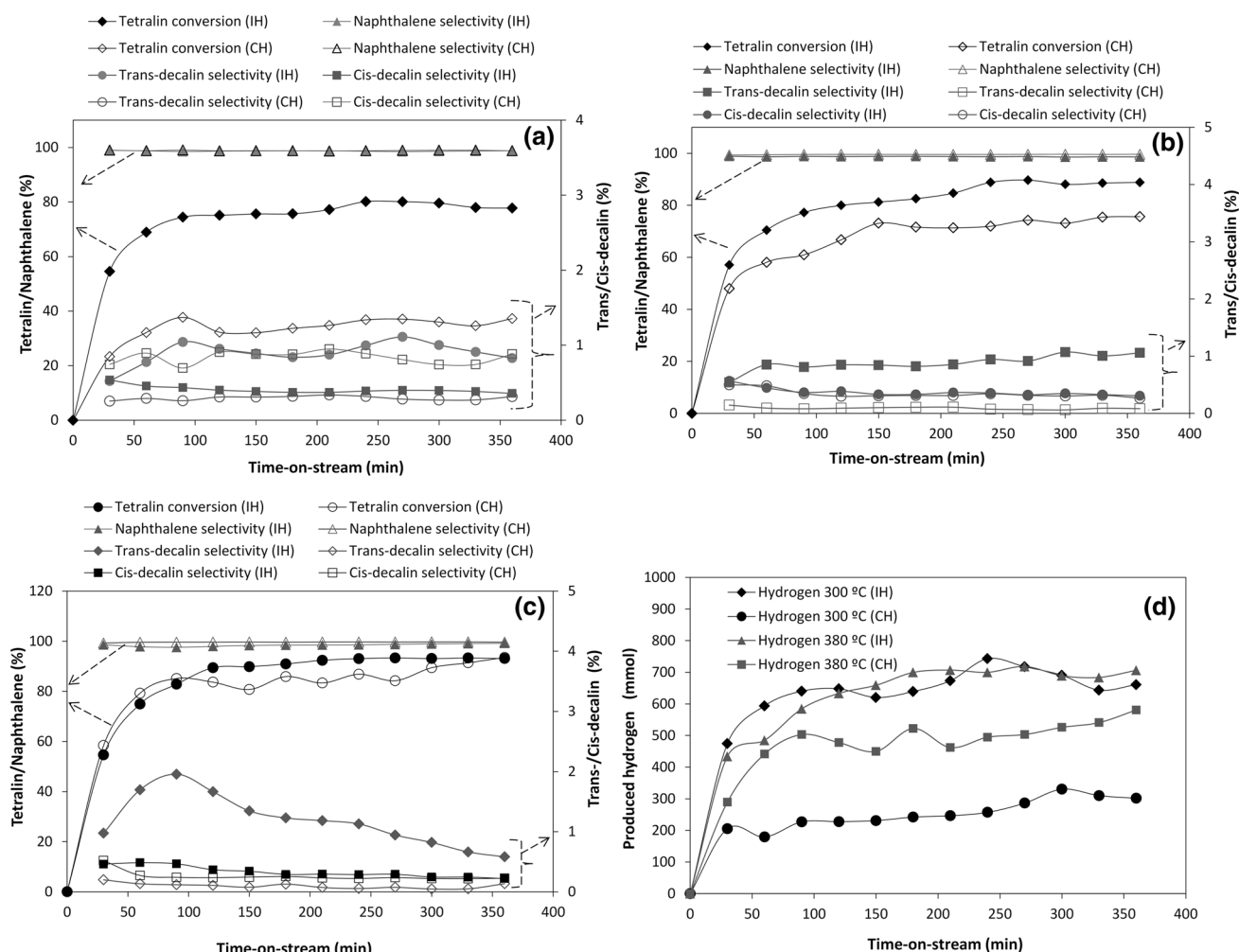


**Fig. 8** Catalyst bed temperature for IH and CH at temperature 300 °C, CTSBR 70% (v/v), LHSV 0.75 h<sup>-1</sup>, pressure 18 barg and 200 mL min<sup>-1</sup> nitrogen flow

Under IH, heat flows from the steel balls to the catalyst pellets and the surrounding fluid, while, with CH it flows from the reactor wall to the surrounding fluid and to the catalyst. The heat generated within the catalyst bed by the steel balls is rapidly transferred to the catalyst and the surrounding fluid because of their intimacy. In the light of this, the actual reaction temperature at the surface of catalyst should be about the same as the surrounding fluid. In other words, the reaction occurred nearer to, or at, the desired temperature at the surface of catalyst, whereas with CH, heat is transferred from the surrounding fluid to the catalyst which increases the temperature gradient between the fluid and the catalyst. Hence, the temperature at the surface of the catalyst was about 5 °C lower than the desired experimental temperature (300 °C).

### 3.6.2 Conversion, Selectivity and Liberated Hydrogen

Figure 9 shows tetralin conversion, produced hydrogen, and selectivity for naphthalene and *trans/cis*-decalins using IH and CH methods at 300 °C, 350 °C and 380 °C. All the experimental results show catalyst start up effect due to wetting and diffusion of reactants and products; hence, the conversion increases with time until steady state is achieved in the reactors. A similar observation has been previously reported in other works [29]. At the three temperatures investigated, tetralin showed superior conversion when the catalytic dehydrogenation was carried out under IH compared to CH method. This remarkable difference in the conversion of tetralin between IH and CH can be clearly observed. This suggests that the temperature between the catalyst and the surrounding fluids exert pronounced effect on the conversion of tetralin through dehydrogenation to mainly hydrogen gas and naphthalene. The dehydrogenation of tetralin under IH



**Fig. 9** Tetralin dehydrogenation conventional heating (CH) against induction heating (IH) at **a** 300 °C, **b** 350 °C, **c** 380 °C and **d** produced hydrogen due to naphthalene formation at pressure 18 barg, LHSV 0.75 h<sup>-1</sup>, CTSBR 70% v/v and gas flow rate of 200 mL min<sup>-1</sup> (N<sub>2</sub>)

reached 80% tetralin conversion at 300 °C, 88% at 350 °C and 93% at 380 °C, whereas at the same conditions the reaction under CH achieved 37% (300 °C), 73% (350 °C) and 86% (380 °C) respectively (Fig. 9a–c). Although, the IH showed superior tetralin conversion, the difference in tetralin conversion under IH and CH decreases as the reaction temperature increases from 300 to 380 °C. The results show that to achieve comparable tetralin conversions, the CH reaction needs to be operated at 50 °C or higher temperature than that of the IH. Hence, the conventionally-heated showed similar tetralin conversion at 300 and 380 °C to that achieved with IH at 250 and 300 °C (Figs. 5a, b, 9a, c).

Converse to the above trends, no significant difference was observed for naphthalene selectivity under IH and CH methods, selectivity greater than 98% was achieved for all the investigated temperatures. Under IH, a thermally stable *trans*-decalin was produced more than unstable *cis*-decalin while under CH more *cis*-decalin was produced. This can be attributed to the difference in temperature at the surface of the catalyst and the activity induced by the heating technique. At 300 °C, the selectivity of *trans* and *cis*-decalins under CH and IH were mirror opposite. Whilst at 350 and 380 °C the selectivity of *cis*-decalin was approximately the same for CH and IH. However, more hydrogen was liberated from tetralin when the reaction was carried out under IH than CH (Fig. 9c).

Thermodynamically, a system that generates heat from within favours tetralin conversion and hydrogen evolution due to dehydrogenation, compared with a system in which the catalyst bed function as a heat sink (Fig. 8). The activity of the catalyst under IH would have been enhanced in addition to the thin temperature gradient between the catalyst and the surrounding fluid. Polarization of reactant molecules, improved catalyst activity, and enhanced molecular diffusion or transport of species in the reaction medium have been proposed as some of the non-thermal effects of electromagnetic field on heterogeneous catalysis carried out under inductive or microwave heating [22]. These non-thermal effects could have improved the activity of the catalyst under IH. The closeness of the steel balls to the catalyst pellets induced rapid heat transfer in the inductive heated catalytic bed which would have promoted faster products (naphthalene, *trans* and *cis* decalins) desorption from the catalyst active sites and lower the strong adsorptive energy of naphthalene [22, 32]. This condition could have increased conversion of tetralin and dehydrogenation under IH. Hence, the low tetralin conversion observed under CH can be attributed to the effect of slow desorption of produced naphthalene from the catalyst surface due to the large temperature gradient between the catalyst and the surrounding fluid (Fig. 8). This could have created heat and mass transfer effect which decrease the catalyst activity under CH [32]. In the case of IH with steel balls, the steel balls rapidly transfer heat to the

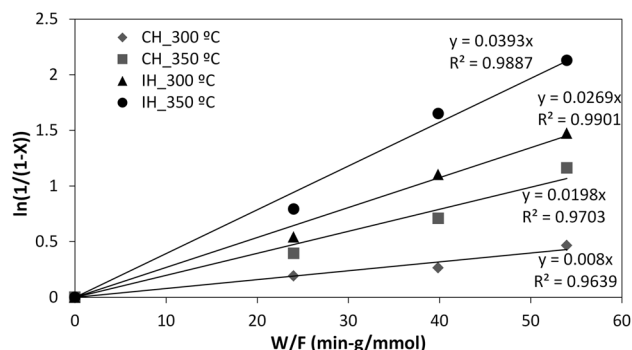
surface of the catalyst and the bulk solvent whereas in CH heat transfer from the bulk solvent to the catalyst is slow (Fig. 8). Hence, under IH naphthalene desorption from the catalyst active sites is enhanced and the strong adsorptive energy of aromatic hydrocarbons lowered [22].

### 3.6.3 First-Order Kinetic Plot

Figure 10 shows the plot of  $\ln(1/(1-X))$  against  $W/F$  for IH and CH systems. The rate constants under IH were higher than those of conventional system at the same reaction temperature, which means the dehydrogenation rate is higher with inductive than CH. This is in agreement with the observation shown in Fig. 9, which affirms that the rate of reaction is higher under IH than CH.

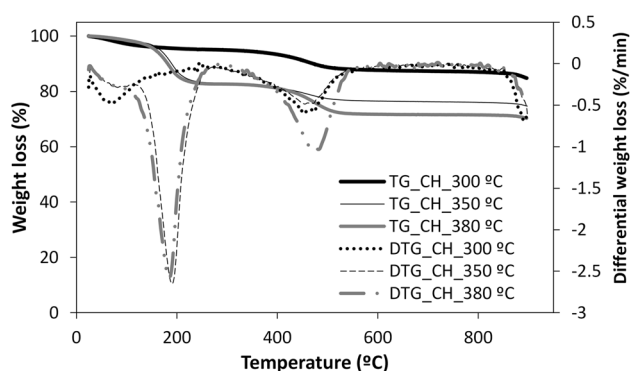
Due to the lower temperatures experienced at the catalyst surface with CH system (i.e., the actual temperature in the catalyst bed is lower than the experimental temperature as shown in Fig. 8), the kinetics are slower compared to that observed with IH. Additionally, the activity of the catalyst could have been limited by adsorbed naphthalene product under CH. The rate constant under CH at 350 °C ( $\sim 0.020 \text{ min}^{-1}$ ) is closely comparable to  $0.027 \text{ min}^{-1}$  obtained under IH at 300 °C (Fig. 6a), which is in agreement with tetralin conversion results shown in Fig. 5b (IH at 300 °C) and Fig. 9b (CH at 350 °C).

Figure 11 shows the TGA of the catalyst after reaction under CH for 300–380 °C. The coke content of the catalyst after 6 h of experiments is as follows: 8.2% (300 °C), 13.6% (350 °C) and 16.4% (380 °C). Compared to IH, coke formation was lesser because the amount of condensed naphthalene product under CH is lower than that produced under IH at the same experimental conditions. Additionally, the improved catalytic activity as well as increased rate of reaction under IH could have also contributed to the high coke formation observed.



**Fig. 10** First-order kinetic plot using Eq. 1 for IH and CH at 300 and 350 °C at pressure 18 barg, LHSV  $0.75 \text{ h}^{-1}$ , CTSBR 70% v/v and gas flow rate of  $200 \text{ mL min}^{-1}$  ( $\text{N}_2$ )





**Fig. 11** TGA of the used catalyst after 6 h experiment at 300, 350 and 380 °C under conventional heating at pressure 18 barg, LHSV 0.75 h<sup>-1</sup>, CTSBR 70% v/v and gas flow rate of 200 mL min<sup>-1</sup> (N<sub>2</sub>)

## 4 Conclusion

Tetralin dehydrogenation as a hydrogen source for underground catalytic upgrading of heavy oil was studied in a fixed-bed reactor that mimics the catalyst packing around the horizontal production well (CAPRI) of the THAI process under induction heating at 300–380 °C, 18 bar, 0.75 h<sup>-1</sup> and 70% (v/v) CTSBR using NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst. The results were compared to those achieved under CH. It was found that under the same operating conditions, higher tetralin conversion and more hydrogen liberation was observed in the inductive-heated system compared with those achieved with the conventional system. Additionally, the catalyst benefited from enhanced activity under the IH because of the non-thermal effect of the eddy current and magnetic fields. The temperature gradient between the surrounding fluid and catalyst was larger under conventional-heated system than inductive-heated counterpart. At 350 °C about 88% tetralin conversion was observed, 0.605 mol of tetralin produced about 0.876 mol of hydrogen mainly through dehydrogenation to naphthalene. This liberated hydrogen has the potential to promote hydroprocessing reactions when combined with in situ catalytic upgrading of heavy oil provided the partial pressure of hydrogen is favourable.

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## Compliance with Ethical Standards

**Conflict of interest** The authors declare no conflict of interest.

**Ethical Approval** This paper has been prepared in compliance with Ethical Standards. The corresponding author confirms this paper conforms to ethical standards and the project from which it is derived was granted ethical approval from the University of Birmingham. No humans or animals were used in the course of this research.

**Informed Consent** The corresponding author has the informed consent of all co-authors in submitting this paper.

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